

AFRL-ML-WP-TP-2006-406

**HIGH-TEMPERATURE REUSABLE
SHAPE MEMORY POLYMER
MANDRELS (PREPRINT)**



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MARCH 2006

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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YY) March 2006		2. REPORT TYPE Conference Paper Preprint		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE HIGH-TEMPERATURE REUSABLE SHAPE MEMORY POLYMER MANDRELS (PREPRINT)				5a. CONTRACT NUMBER FA8650-05-5300	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER N/A	
6. AUTHOR(S) Matthew C. Everhart Beth A. Knapp				5d. PROJECT NUMBER N/A	
				5e. TASK NUMBER N/A	
				5f. WORK UNIT NUMBER N/A	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Cornerstone Research Group, Inc. 2750 Indian Ripple Road Dayton, OH 45440				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Materials and Manufacturing Directorate Air Force Research Laboratory Air Force Materiel Command Wright-Patterson AFB, OH 45433-7750				10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL-ML-WP	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-ML-WP-TP-2006-406	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES <p>Conference paper preprint submitted to the SPIE-sponsored International Society for Optical Engineering for publication in the Optics and Photonics 2006 Conference Proceedings.</p> <p>This work resulted in whole or in part from Department of the Air Force contract number FA8650-05-5300. This paper contains color. PAO Case Number: AFRL/WS 06-0298, 6 Feb 06.</p>					
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15. SUBJECT TERMS <p>High-Temperature, Polymer, Mandrels, Memory</p>					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT: SAR	18. NUMBER OF PAGES 16	19a. NAME OF RESPONSIBLE PERSON (Monitor) Frances Abrams 19b. TELEPHONE NUMBER (Include Area Code) N/A
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			

High-Temperature Reusable Shape Memory Polymer Mandrels

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ABSTRACT

Cornerstone Research Group, Inc. (CRG) has demonstrated the feasibility of filament winding complex-curved composite shapes on shape memory polymer (SMP) mandrels. SMPs can exhibit a radical change from a rigid polymer to a flexible, elastic state, and then back to a rigid state under thermal stimuli. SMP mandrels for filament winding and fiber placement allow for a quick, easy, reusable, and low-cost mandrel system. CRG has recently improved the SMP mandrel technology by adding a high-strain fiber reinforcement (HSFR) that both raises the toughness of the SMP and allows the SMP to elongate up to 150 percent. The resulting material can produce mandrels durable enough to withstand multiple use in high production rate manufacturing. This paper will demonstrate and discuss the feasibility of HSFR-SMP mandrels for filament winding and fiber placement and recent developments in CRG's SMP mandrel technology, including the fabrication of larger parts.

Keywords: filament winding, tooling materials, fiber reinforcement

1. INTRODUCTION

In 2004, Cornerstone Research Group, Inc. (CRG) developed the materials and processing technologies needed for a mandrel system capable of the fabrication of complex-curved composites. This mandrel system is a low-cost system that quickly and easily transforms into various detailed shapes, which then function as a traditional mandrel that is dimensionally accurate, autoclave-tolerant, rapidly removable, and reusable. The original mandrel system exhibited great versatility and functionality; however, it was only capable of cure temperatures to 40 degrees Celsius (40°C). This limited the mandrel system to use with resins that partially or fully cure at or near room temperature. Although SMP mandrels offer many opportunities at this low temperature activation point, they are excluded from use in many aerospace composite manufacturing processes. Most aerospace composite resin systems have cure cycle temperatures reaching 250 to 350°F (121 to 176°C). To develop a mandrel system capable of high temperature cure cycles, several technical hurdles needed to be overcome. This paper will discuss the difficulties incurred, the solutions, and the resulting new material system that is capable of 350° F (176°C) cure.

1.1. SMP Mandrels Background

Cornerstone Research Group, Inc. (CRG) has demonstrated the feasibility of using shape memory polymers (SMPs) for tooling applications, such as mandrels for composite fabrication. SMP mandrels have unique properties due to SMPs ability to exhibit a radical change from a rigid polymer to a very flexible elastic state, then back to a rigid state again, under thermal stimuli. SMP mandrel system offers several benefits in terms of manufacturing composite parts over conventional methods. The most notable is the SMP mandrel systems extraction process.

After a composite part is fabricated on a mandrel, either by filament winding, fiber placement, or hand lay-up, the mandrel in most cases will be extracted. Certain geometries of composite parts are problematic for mandrel extraction. The relatively simple process of wrapping a mandrel with fibers becomes complicated when the composite part is comprised of a compound-curved shape. Simply stated, a mandrel must be designed to remain rigid during winding and curing, yet be able to collapse to allow its extraction. Internal mandrels for complex-curved composites require extensive design considerations to ensure that the mandrel can be removed after the composite is cured. This makes mandrels very expensive to develop, difficult to fabricate, and time-consuming to remove from a cured part. Each composite part requires the design of a unique mandrel that is removable without damaging the composite part. Multi-piece metal mandrels and water-soluble mandrels are the two primary types of mandrels used for complex parts.

Multi-piece metal mandrels are a complex system of metal pieces that fit together to collectively form a desired shape. After fabrication, the metal pieces can be disassembled and removed from inside the composite. Large amounts of time and energy are invested into the design of multi-piece metal mandrels to ensure that every piece can be safely extracted from the fabricated composite part. Also, the disassembly and reassembly of the mandrels is very labor-intensive. These factors combine to make fabrication with multi-piece metal mandrels costly.

Water-soluble sand or salt mandrels are another type of mandrel offering high precision. A metal support rod runs through the center of a mass of bonded sand or salt that forms the mandrel shape. The filament is wound onto the soluble mandrel and then cured. After the composite part has cured, water is injected inside the part to loosen the sand or salt from the cured part. When the soluble mandrel has been flushed away, the supporting rod is removed. However, the soluble mandrels are often used only once and discarded, requiring disposal of hazardous or noxious waste materials. Soluble mandrel fabrication is also costly and time-consuming. Advances in mandrel technology would significantly benefit the composite manufacturing industry.

SMP mandrels are rigid throughout the composite fabrication and the cure. The mandrels are made of a thermoset plastic resin and are reinforced by a high-strain fabric material. This translates to a mandrel that is extremely durable and more rigid than thermoplastic tools. After the composite part has been cured on the rigid tool the SMP mandrel is activated by thermal stimuli, it becomes very soft and rubber like. This transition allows for gentle and simple extraction.

1.2. Shape memory polymer (SMP) background

First introduced in the United States in 1984, SMPs are polymers whose qualities have been altered to give them dynamic shape “memory” properties. Under thermal stimuli, SMP can exhibit a radical change from a rigid thermoset plastic to a highly flexible, elastic state, then return to a rigid state again. In its elastic state, SMP will recover its “memory” shape if left unrestrained. The “memory,” or recovery, quality comes from the stored mechanical energy attained during the reconfiguration and cooling of the material. SMP’s ability to change stiffness modulus and shape configuration at will makes SMP ideal for applications requiring lightweight, dynamic, and adaptable materials.

Unlike a shape memory alloy (SMA), SMP exhibits a radical change from a normal rigid polymer to a flexible elastic and back on command, a change that can be repeated without degradation of the material. The SMP transition process is a thermomolecular relaxation rather than a thermally-induced crystalline phase transformation, as with SMA. In addition, SMP demonstrates much broader range and versatility than SMA in shape configuration and manipulation.

SMP is a fully formable thermoset. It exhibits characteristics of both an elastomer and a thermoplastic, depending on temperature. While rigid, SMP demonstrates the strength-to-weight ratio of a rigid polymer; however, normal rigid polymers under thermal stimulus simply flow or melt, and they have no “memorized” shape to which they return. While heated and pliable, SMP has the flexibility of a high-quality, dynamic elastomer, tolerating up to 200% elongation; however, unlike normal elastomers, SMP can be reshaped or returned quickly to its memorized shape and subsequently cooled into a rigid plastic. Figure 1 shows the elastic modulus of SMP in relation to temperature. Figure 2 shows a chart of storage modulus (stiffness) versus temperature, showing the initial range of CRG’s patented styrene SMP with activation temperatures customizable to between 110°F and 220°F (47°C to 106°C).

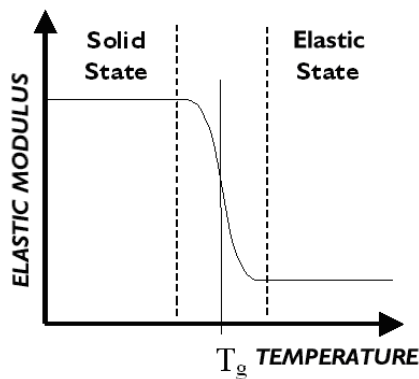


Figure 1. SMP elastic modulus versus temperature

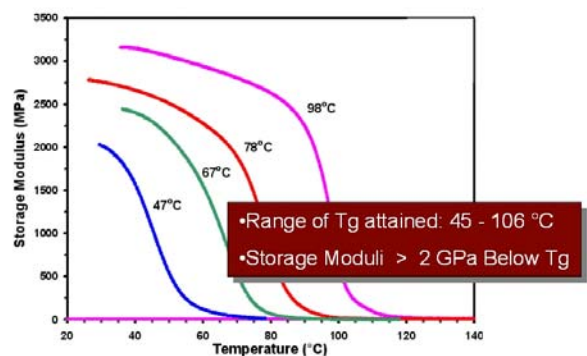


Figure 2. DMA graph of various styrene SMP storage moduli

1.3. High-strain fiber reinforcement (HSFR) background

To reduce the cost of SMP mandrel tooling for high production rate manufacturing, the tooling must be capable of being reused multiple times. Although

SMP mandrels have demonstrated prototype aerospace-grade composite fabrication, they lack the durability to endure a traditional high production rate manufacturing environment. Generally, polymer tooling lacks the toughness to undergo an abusive factory environment while maintaining high dimensional tolerance. Tooling in typical manufacturing processes will experience harsh conditions during composite fabrication over the life time of the tool. The tooling will endure impacts, abrasions, thermal cycling, and other abuse that will cause cuts, scrapes, and other damage. This damage, which is primarily due to the mechanical properties of the polymer, vastly reduces the life of a tool. Cuts, scrapes, and impacts cause points of high stress, leading to crack propagation and polymer failure. These abuses can be combated by toughening the polymer through the addition of an elastomeric material into the polymer matrix, or the addition of fiber reinforcement. Toughening increases the ability to absorb and dissipate impact energy and mitigate crack propagation by distributing the force over a greater area. Glass and carbon fiber are currently used as reinforcements in polymer matrix composites. The fibers increase the toughness of the composite by effectively transferring a point force across the fiber length and distributing the applied forces into both the polymer matrix and the other fibers.

Although both are effective methods of toughening, neither are useful for toughening SMP for mandrel applications. These methods negatively impact material properties that are critical for mandrel applications. The addition of an elastomeric material to increase toughness results in a material that exhibits a lower modulus than the base polymer. The lower modulus reduces the capability of the tool to maintain the high dimensional tolerances required in an aerospace composite fabrication. The addition of reinforcement materials such as glass or carbon fiber, results in a composite that exhibits high strength; however, it would not be capable of high elongation. The mechanical property of 200% elongation and recovery is the material property that offers the greatest advantage to SMP mandrels.

CRG developed a high-strain fiber reinforcement (HSFR) system to toughen and increase durability of the SMP mandrel material. The HSFR material allows forces to be distributed thought the SMP while below its glass transition temperature, and also allows the SMP to elongate effectively when the material is above its glass transition temperature. Figure 3 shows a HSFR composite fabricated by CRG.

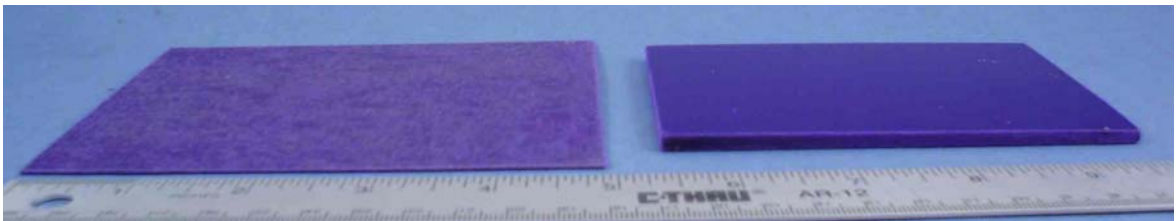


Figure 3: HSFR composites of various layers.

The HSFR-SMP composite materials have shown large increases in toughness compared to the neat SMP materials. The average increase in toughness is shown in Figure 4. This data shows that a single layer of reinforcement can increase the toughness by more than 200%.

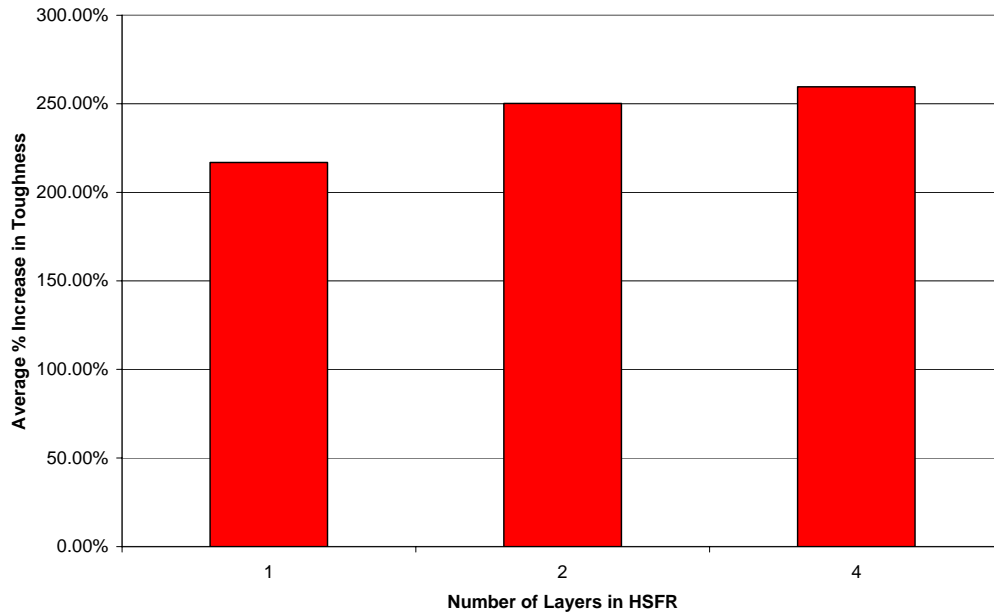


Figure 4: Increase in toughness of HSFR-SMP materials compared to baseline SMP material.

2. HIGH TEMPERATURE SHAPE MEMORY POLYMER MANDREL TECHNOLOGY

2.1 Technical Challenges

The lower temperature SMP Mandrels are fabricated using CRG's most mature Veriflex™ resin system, a styrene-based resin with an activation temperature of approximately 65°C and a high-strain reinforcement fabric. The high-strain reinforcement fabric was used to increase the strain capabilities of the SMP composite, thus increasing toughness and limiting tear propagation. To develop a mandrel system that is capable of manufacturing 350°F (176°C) cured aerospace parts, the SMP's activation temperature would need to be greater than the cure temperature. Otherwise, the mandrel would become soft before the part had become rigid. Also, to meet the durability for a manufacturing process, the high strain fiber reinforcement would need to remain incorporated.

The first major hurdle that needed to be overcome was the identification of a new high temperature SMP resin. Through formulation changes, an SMP's activation temperature can be altered to a wide range of desirable temperatures. This range of temperatures, however, is set by the characteristics of the base polymer system. Unfortunately, styrene SMP has an upper limit of 106 °C, and for this application a temperature range from 160°C to 220°C activation temperature was desired. This is 30 to 40°C above the highest cure temperature, which ensures that there is no creep of the mandrel during the cure cycle. A different polymer system needed to be identified, reformulated to exhibit SMP properties, and fabricated into a mandrel. This high-temperature of 220°C left a limited number of candidate polymers, and most were very difficult to reformulate.

The second hurdle that needed to be overcome was the HSFR material that is used in the styrene mandrel system was not capable of being used at 220°C. Differential scanning calorimetry (DSC) was used to determine the melting point of the reinforcement

material. The drop in the heat flow on the plot of heat flow versus temperature indicates a phase change. The graph seen in Figure 5 shows a phase change at 205°C which indicates this materials melting point.

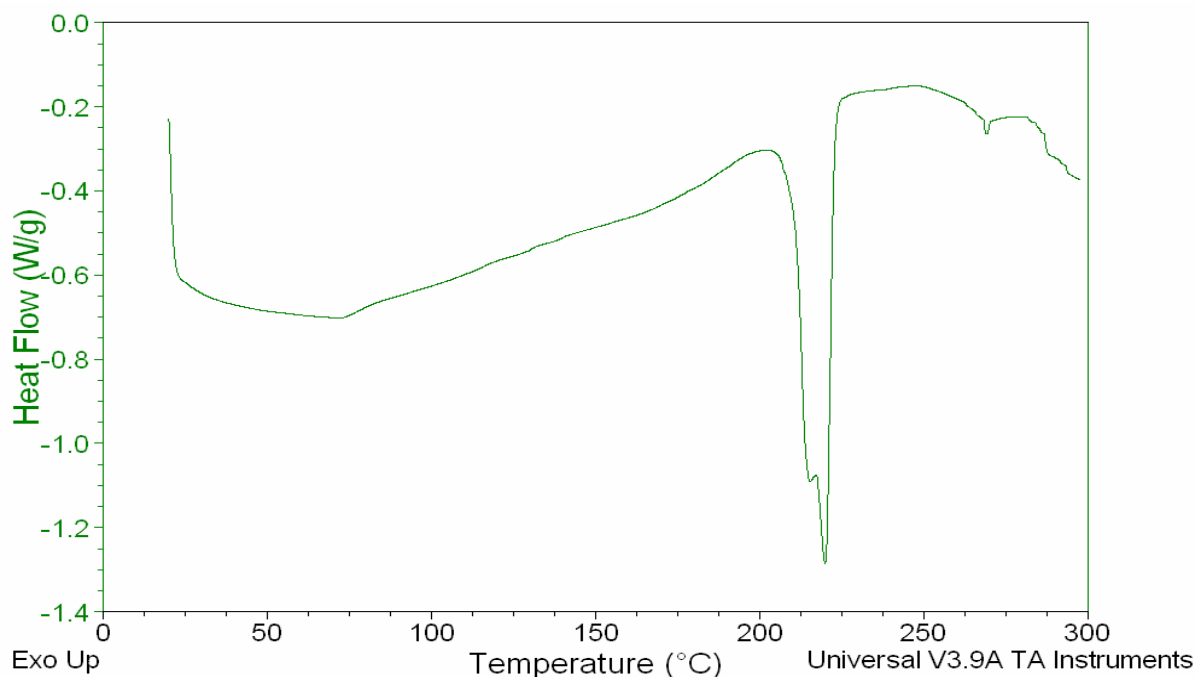


Figure 5. A differential scanning calorimetry (DSC) graph of HSFR material; melting point 205°C.

2.2 Cyanate Ester Shape Memory Polymer

CRG developed a patent-pending cyanate-based ester SMP that provides shape memory performance in a high-temperature material.

Cyanate ester resins are a unique class of prepolymers that contain highly reactive cyanate (-OCN) functional groups. These resins cure via a cyclotrimerization reaction, in which three cyanate functional groups react to form a ring. This mechanism creates a very high cross-link density in the cured material, producing the excellent thermomechanical properties of these resins.

The cyanate ester SMP (Figure 6) is based on a formulation of monomers and reactive property modifiers. By controlling the concentrations of the components, the resulting polymer can have cross-linking densities varying from those of a dense thermoset to those approaching a linear thermoplastic. The degree of this cross-linking within the polymer determines both the strain recovery properties and the glass transition temperature (T_g) of the material. The T_g is the threshold at which the SMP changes from rigid to elastic in response to thermal stimulus (heating).



Figure 6: Cyanate ester shape memory polymer exhibiting shape recovery from deformed configuration (left) to memorized configuration (right) when activated by heat

Characterization by dynamic mechanical analysis (DMA) provides data on storage and loss moduli. The storage modulus plot depicts the stiffness of the material with respect to temperature. The steep decline of the curve represents the temperature range over which the polymer is softening. The inflection point of that curve, located close the middle point of the steep slope, is an estimate of T_g . The loss modulus plot displays the energy lost to the material when it endures a mechanical stress. As the temperature increases, the polymer molecules begin to obtain greater and greater energy, allowing some internal mobility to the material's structure. The peak of the loss curve is representative of the onset of segmental mobility in the polymer, indicative of the T_g . The following plots both indicate that the baseline cyanate ester SMP has fine tunable temperature range from T_g of 135°C (Figure 7) to 230°C (Figure 8)

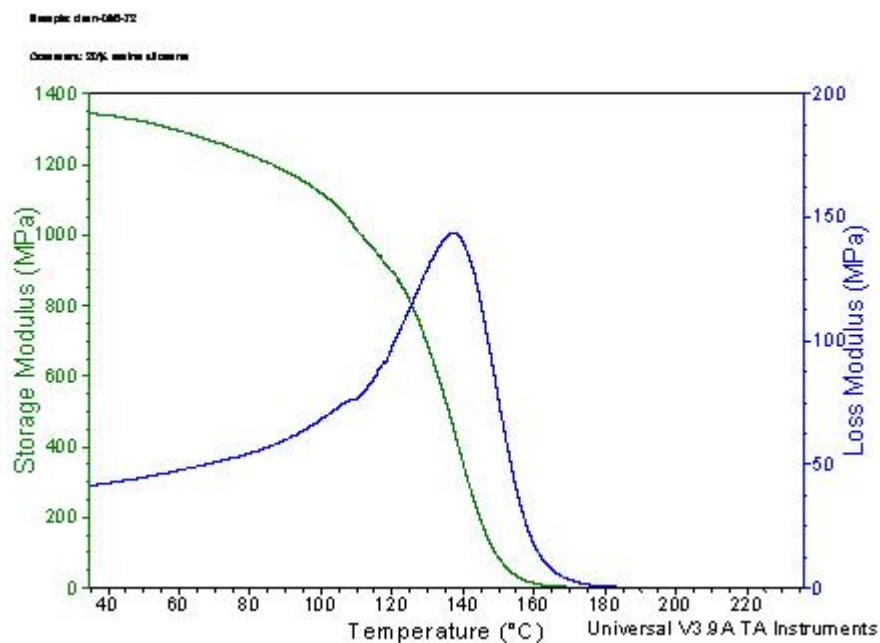


Figure 7. DMA graph of 135 °C T_g cyanate ester SMP storage modulus

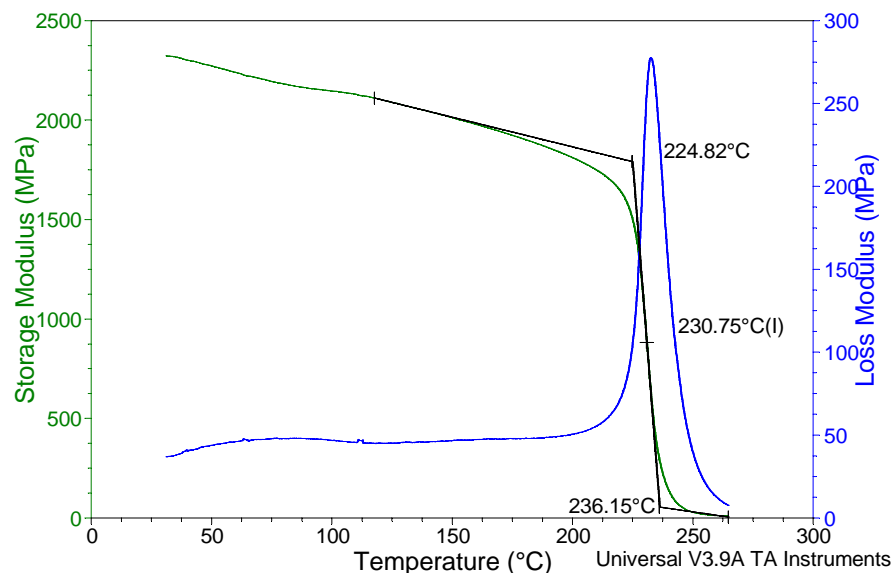


Figure 8. DMA graph of 230 °C T_g cyanate ester SMP storage modulus

Cyanate ester SMP materials have been developed to a point of functionality for a high-temperature mandrel system. The goal of this research was to formulate and characterize a new cyanate ester SMP that has properties conducive to mandrel use. The temperature range was the most important mechanical property. Other favorable properties include:

- Elongation greater 40 %
- Excellent strain recovery - 100% recovery
- Low coefficient of thermal expansion (CTE)
- Low density

2.3 High Performance High Strain Fiber Reinforcement

A high performance HSFR material was identified from a commercial supplier. The material is capable of sustained exposure to temperatures up to 250 °C as shown by the differential scanning calorimetry (DSC) plot in Figure 9.

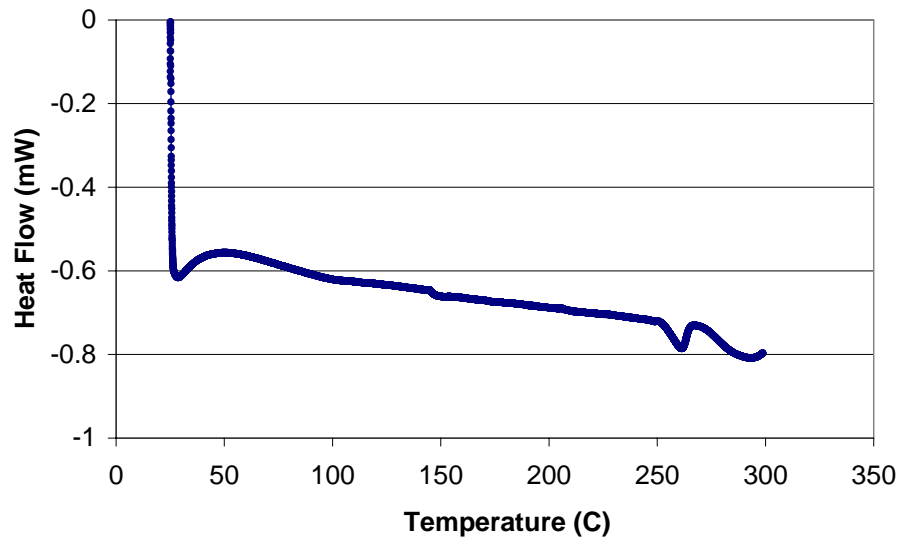


Figure 9. Differential scanning calorimetry (DSC) graph of HSFR material.

The new HSFR material processes well with the resin. A sample of the combined materials can be seen in Figure 10. The material also allows the base SMP material to elongate to the 40% maximum.

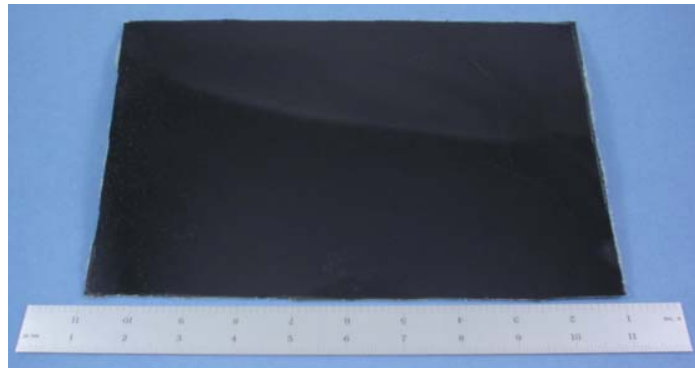


Figure 10. Cyanate ester SMP with HSFR reinforcement.

2.4 Conclusions

CRG developed an SMP mandrel system for the fabrication of high temperature (350°F/176°C), complex-curved composites. This system is based on a patent-pending cyanate ester SMP material that was developed at CRG and a high performance HSFR material. The new combination of materials work well together to produce a hard, durable material for a high temperature mandrel system. The cyanate ester SMP offers a lot of versatility in temperature formulations. The resin system can be tailored from 135°C to 230°C. This broad range of temperatures will allow the mandrel systems to be activated at desired set points. The only apparent drawback to the new system is a reduction in maximum elongation from 100% to 40%. This will need to be considered in designing future mandrel systems.